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# A Thermodynamic Property Model for the R-134a/245fa Mixtures

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## ABSTRACT

A thermodynamic property model explicit in the Helmholtz energy is presented for the R-134a/245fa mixtures. A multi-fluid approximation based on pure-fluid Helmholtz energy equations of state forms the basis of the property model. The Helmholtz energy of the mixture is expressed as the sum of the ideal gas contribution, the compressibility contribution (real fluid contribution), and the contribution from mixing to represent the deviation from ideal mixtures. The independent variables are the temperature, molar volume, and composition. The model can be used to calculate all thermodynamic properties of the mixtures at various compositions. The estimated uncertainties in calculated properties from the model are  $\pm 0.2$  % for the bubble and dew point pressures and  $\pm 0.24$  % for the liquid and vapor densities. The critical parameters of the mixtures are properly represented with the model. The calculated critical temperatures correspond to experimental values within  $\pm 0.5$  K.

## 1. INTRODUCTION

Table 1 summarizes characteristic properties of 1,1,1,2-tetrafluoroethane (R-134a) and 1,1,1,3,3-pentafluoropropane (R-245fa). Due to their far from negligible global warming potentials (GWPs), both refrigerants will be phased out in the near future. Research and development for alternatives for the refrigerants are ongoing mainly in the United States and Japan, and some candidates have been produced; for example, 2,3,3,3-tetrafluoropropene (R-1234yf) for R-134a and cis-1,3,3,3-tetrafluoropropene (R-1234ze(Z)) for R-245fa. However, a highly promising alternative, i.e., an alternative with high performance, low production cost, no flammability, and no toxicity, has not so far been proposed. Therefore, it is considered that in at least the next decade the refrigeration industry still uses R-134a, R-245fa, and their mixtures for refrigeration systems or heat pumps. Recently, some manufacturers have produced high performance heat pumps using the R-134a/245fa mixtures (Oue and Okada, 2013). Pure R-245fa has also been paid attention for the working fluid of organic Rankin cycles (ORCs) for low temperature heat sources (Masheiti et al., 2011; Takahashi et al., 2013).

This work presents a thermodynamic property model for the R-134a/245fa mixtures. At this time an accurate property model are not available for the mixtures. The model presented here is capable of calculating all thermodynamic properties of the mixtures with sufficient accuracies for the refrigeration cycle analysis.

## 2. EXPERIMENTAL DATA

The only property information on the R-134a/245fa mixtures available from the public domain are the vapor-liquid equilibrium (VLE) measurements reported by Bobbo et al. (2001). The VLE measurements include 31 data points at temperatures from 293 K to 313 K. This work has recently measured the  $pvTx$  properties of the mixtures at three different compositions. The distributions of the  $pvTx$  data are shown in Fig. 1. Although the  $pvTx$  data cover both single phase region (gas and liquid) and two phase region, only the data in the single phase region were incorporated

**Table 1: Characteristic properties of R-134a and R-245fa – All properties except GWPs are cited from REFPROP (Lemmon et al., 2013). The GWPs are adopted from IPCC Fourth Assessment Report (Solomon et al., 2007)**

Property	R-134a	R-245fa
Molar mass (g mol <sup>-1</sup> )	102.03	134.05
Critical temperature (K)	374.21	427.16
Critical pressure (MPa)	4.0593	3.651
Critical density (kg m <sup>-3</sup> )	511.9	516.08
Normal boiling point (K)	247.08	288.29
Acentric factor	0.3268	0.3776
100yr-GWP	1430	1030

**Table 2: Experimental data of the critical temperatures and densities of the R-134a/245fa mixtures – Values in parentheses are calculated values from the KW1 model with the optimum parameters.**

$x^a$	$M$ (g mol <sup>-1</sup> )	$T_c$ (K)	$\rho_c$ (kg m <sup>-3</sup> )
0.1	129.97	422.07 (421.88)	530 (501.08)
0.3	122.52	411.80 (411.47)	535 (502.08)
0.5	115.87	400.44 (400.94)	532 (504.73)

<sup>a</sup>Mass fraction of R-134a

in the model development. The detail of the  $pvTx$  property measurement, including numerical values, experimental apparatus, and uncertainties, will be presented elsewhere (Higashi and Akasaka, 2014). In addition to the  $pvTx$  data, this work measured the critical temperature, the critical density, and the saturated liquid and vapor densities, in advance of the model development. This measurement employed the same apparatus as that used in our previous works (Higashi et al., 2010; Akasaka et al., 2013). The experimentally determined critical temperature and density are given in Table 2, as well as calculated values from the property model developed in this work.

### 3. THERMODYNAMIC PROPERTY MODEL

A multi-fluid approximation explicit in the reduced Helmholtz energy forms the basis of the property model developed in this work. The property model expresses the reduced Helmholtz energy of a mixture  $\alpha$  as

$$\frac{a}{RT} = \alpha = \alpha^{\text{idmix}} + \alpha^E, \quad (1)$$

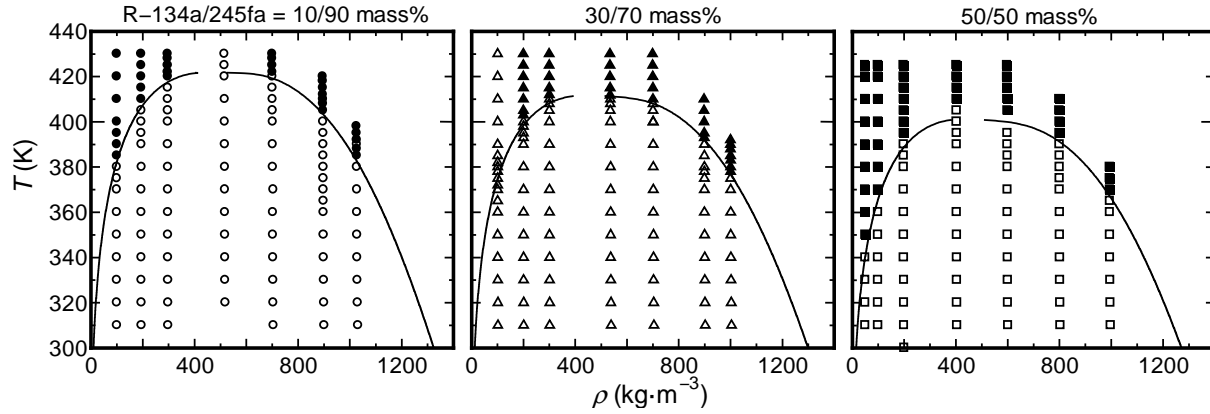
where  $a$  is the molar Helmholtz energy of the mixture,  $T$  is the mixture temperature,  $R = 8.3144621 \text{ J mol}^{-1} \text{ K}^{-1}$  (Mohr et al., 2012) is the universal gas constant,  $\alpha^{\text{idmix}}$  is the ideal mixture contribution, and  $\alpha^E$  is the contribution from mixing. For a binary mixture,  $\alpha^{\text{idmix}}$  is calculated from

$$\alpha^{\text{idmix}} = x [\alpha_1^\circ(T, v) + \alpha_1^r(\tau, \delta) + \ln x] + (1 - x) [\alpha_2^\circ(T, v) + \alpha_2^r(\tau, \delta) + \ln (1 - x)], \quad (2)$$

where  $v$  is the mixture molar volume,  $\tau$  and  $\delta$  are the reduced mixture temperature and volume,  $\alpha_i^\circ$  and  $\alpha_i^r$  are the ideal-gas part and residual part of the Helmholtz energy of component  $i$ , and  $x$  is the mole fraction of the first component. For calculations of  $\alpha_i^\circ$  and  $\alpha_i^r$ , this work used the equation of state developed by Tillner-Roth and Baehr (1994) for R-134a and that by Akasaka et al. (2014) for R-245fa.

The reduced mixture temperature and volume are defined as

$$\tau = \frac{T_{\text{red}}(x)}{T} \quad (3)$$



**Figure 1: Distribution of the  $pvTx$  data – Filled symbols indicate data used in the model development.**

and

$$\delta = \frac{v_{\text{red}}(x)}{v}, \quad (4)$$

where  $T_{\text{red}}$  and  $v_{\text{red}}$  are reducing functions for the mixture temperature and molar volume. This work adopted reducing functions presented by Kunz et al. (2007). The functions (KW reducing functions) for a binary mixture have the forms

$$T_{\text{red}}(x) = x^2 T_{c,1} + (1-x)^2 T_{c,2} + 2\beta_T \gamma_T \left[ \frac{x(1-x)}{(\beta_T^2 - 1)x + 1} \right] T_{c,12} \quad (5)$$

and

$$v_{\text{red}}(x) = x^2 v_{c,1} + (1-x)^2 v_{c,2} + 2\beta_v \gamma_v \left[ \frac{x(1-x)}{(\beta_v^2 - 1)x + 1} \right] v_{c,12}, \quad (6)$$

where

$$T_{c,12} = \sqrt{T_{c,1} T_{c,2}}, \quad (7)$$

$$v_{c,12} = \frac{1}{8} (v_{c,1}^{1/3} + v_{c,2}^{1/3})^3, \quad (8)$$

and  $\beta_T$ ,  $\gamma_T$ ,  $\beta_v$ , and  $\gamma_v$  are adjustable parameters.

The contribution from mixing in a binary mixture is empirically represented as

$$\alpha^E(\tau, \delta, x) = x(1-x) F_{12} \alpha_{12}^E(\tau, \delta), \quad (9)$$

where  $\alpha_{12}^E(\tau, \delta)$  is a binary specific or generalized departure function and  $F_{12}$  is an empirical scaling factor used to adjust the magnitude of  $\alpha_{12}^E$  for a mixture of interest. Several departure functions have been proposed by Lemmon and Jacobsen (1999, 2004) and Kunz et al. (2007) for mixtures including hydrocarbons, noble gases, and refrigerants.

This work combined the KW reducing functions with one of the departure functions by Lemmon and Jacobsen and by Kunz et al. Each combination is identified by the designations given in Table 3. For example, the KWR model is the combination of the KW reducing functions and the departure function specified for the R-32/125 mixtures. Such designations follow the fashion of the latest version of REFPROP (Lemmon et al., 2013).

For the total of the 12 combinations listed in Table 3, optimum values of the adjustable parameters were individually determined by the nonlinear least-square fitting to experimental data of the R-134a/245fa mixtures. The best combination was accordingly selected that results in a minimum final sum of squares in the nonlinear fitting.

**Table 3: Combinations of the reducing functions and departure functions**

Designation	Reducing functions	Departure function
KWG <sup>a</sup>	KW	generalized for binary pairs in methane, ethane, propane, n-butane, isobutane, ethylene, nitrogen, argon, oxygen, and carbon dioxide <sup>b</sup>
KWR	KW	specified for R-32 + R-125 mixtures <sup>c</sup>
KWS	KW	specified for R-32 + R-134a mixtures <sup>c</sup>
KWT	KW	generalized for R-125 + R-134a, R-125 + R-143a, R-134a + R-143a, and R-134a + R-152a mixtures <sup>c</sup>
KW0	KW	generalized for methane + n-butane, methane + isobutane, ethane + propane, ethane + n-butane, ethane + isobutane, propane + n-butane, propane + isobutane, and n-butane + isobutane mixtures <sup>d</sup>
KW1	KW	specified for methane + ethane mixtures <sup>d</sup>
KW2	KW	specified for methane + propane mixtures <sup>d</sup>
KW3	KW	specified for methane + nitrogen mixtures <sup>d</sup>
KW4	KW	specified for methane + carbon dioxide mixtures <sup>d</sup>
KW5	KW	specified for nitrogen + carbon dioxide mixtures <sup>d</sup>
KW6	KW	specified for nitrogen + ethane mixtures <sup>d</sup>
KW7	KW	specified for methane + hydrogen mixtures <sup>d</sup>

<sup>a</sup>not used in REFPROP<sup>b</sup>developed by Lemmon and Jacobsen (1999)<sup>c</sup>developed by Lemmon and Jacobsen (2004)<sup>d</sup>developed by Kunz et al. (2007)**Table 4: Optimum parameters and final sum of square**

Mixture model	$\beta_T$	$\gamma_T$	$\beta_v$	$\gamma_v$	$F_{12}$	$S_{\text{final}} \times 10^3$
KWG	1.	1.00372	0.992392	0.998056	0.145638	0.1136
KWR	1.	1.01541	0.992526	1.00950	0.185932	0.4036
KWS	1.	1.01264	0.993027	1.01662	0.539071	0.5048
KWT	1.	1.00717	0.992132	1.00391	0.909890	0.2710
KW0	1.	1.00608	0.993058	1.00117	0.0529635	0.1222
KW1	1.	1.00643	0.992025	1.	0.107754	0.1128
KW2	1.	1.00592	0.993705	1.00213	0.0500026	0.1394
KW3	0.999303	1.00604	0.993438	0.999266	0.120055	0.2690
KW4	0.999366	1.00774	0.992810	0.995019	0.123985	0.2695
KW5	1.	1.00714	0.992583	0.997638	0.0561002	0.1470
KW6	1.	1.00682	0.992581	0.997262	0.057564	0.1379
KW7	1.	0.998221	0.994407	1.01430	0.116853	0.3022

The following objective function  $S$  was used in the nonlinear fitting:

$$S = \frac{1}{n_{p_b}} \sum W_{p_b} X_{p_b}^2 + \frac{1}{n_{p_d}} \sum W_{p_d} X_{p_d}^2 + \frac{1}{n_{\rho}} \sum W_{\rho} X_{\rho}^2 + \frac{1}{n_{T_c}} \sum W_{T_c} X_{T_c}^2 + \frac{1}{n_{v_c}} \sum W_{v_c} X_{v_c}^2,$$

where  $W$  is a weighting factor,  $n$  is the number of experimental data points, and  $X$  is the relative deviation in experimental properties from calculated values. For example,  $X_{T_c}$  is

$$X_{T_c} = \frac{T_{c,\text{exp}} - T_{c,\text{cal}}}{T_{c,\text{cal}}}, \quad (10)$$

where  $T_{c,\text{exp}}$  is an experimental value for the critical temperature and  $T_{c,\text{cal}}$  is a calculated value from the property model. The nonlinear fitting mainly used the vapor-liquid equilibrium (VLE) data and  $pvTx$  property data. In addition

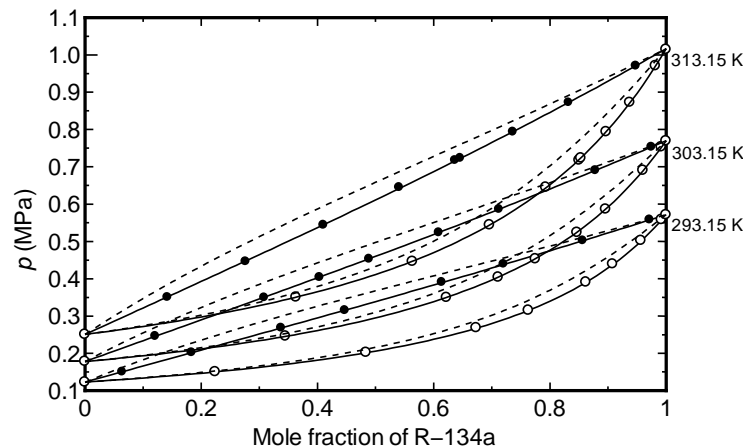
to these data, the fitting incorporated experimental critical parameters given in Table 2 to ensure that the property model represents the critical locus correctly. Since the calculation of the critical parameters of mixtures is extremely involved and often numerically unstable, this work employed the technique presented by Akasaka (2007) in the nonlinear fitting. This technique provides a robust algorithm for the critical point calculations.

Each data point was individually weighted according to type, region, and uncertainty. In this work, typical values for  $W$  were 1 for the bubble point pressure, 0.1 for the dew point pressure, 1 for density, 1 for the critical temperature, and 0.1 for the critical molar volume.

Table 4 shows the optimum values of  $\beta_T$ ,  $\gamma_T$ ,  $\beta_v$ ,  $\gamma_v$ , and  $F_{12}$  and the final sum of square  $S_{\text{final}}$  for each combination. The value of  $\beta_T$  was often kept unity during the nonlinear fitting, which means that the parameter has only a very small effect on the sum of square. The minimum  $S_{\text{final}}$  was obtained from the KW1 model with optimum parameters.

#### 4. COMPARISONS TO EXPERIMENTAL DATA

Fig. 2 shows the isothermal VLE calculated from the KW1 model with the optimum parameters, as well as the experimental data by Bobbo et al. (2001) at 293.15 K, 303.15 K, and 313.15 K. For comparison, the figure includes the VLE obtained from REFPROP, in which the KW0 model is used with estimated parameters. The KW1 model represents very well the experimental VLE data. The average absolute deviations (AADs) in experimental bubble and dew point pressures from calculated values are 0.16 % and 0.18 %, respectively. The deviations are comparable to the experimental uncertainties claimed by Bobbo et al.



**Figure 2: Isothermal vapor-liquid equilibrium of the R-134a/245fa mixtures:**  
 (● ○) Bobbo et al. (2001), (---) REFPROP 9.1 (Lemmon et al., 2013), (—) KW1 model  
 (This work)

Deviations in the experimental densities in the single phase from calculated values are shown in Fig. 3. The AAD in the densities is 0.24 %. This is slightly larger than the experimental uncertainties but acceptable in most technical applications. Most densities are represented within  $\pm 0.5$  %. Deviations up to  $\pm 1$  % are sometimes observed at temperatures above 400 K. Systematic deviations are not observed.

In Fig. 4, phase boundaries obtained from the KW1 model are plotted on the  $T$ - $\rho$  diagram. Experimental saturated liquid and vapor densities are well represented with the model, although the densities were not used in the nonlinear fitting. The critical points calculated from the model nearly correspond to experimentally determined critical point. This is also confirmed in Table 2. The calculated critical temperatures deviate by only  $\pm 0.5$  K from the experimental values.

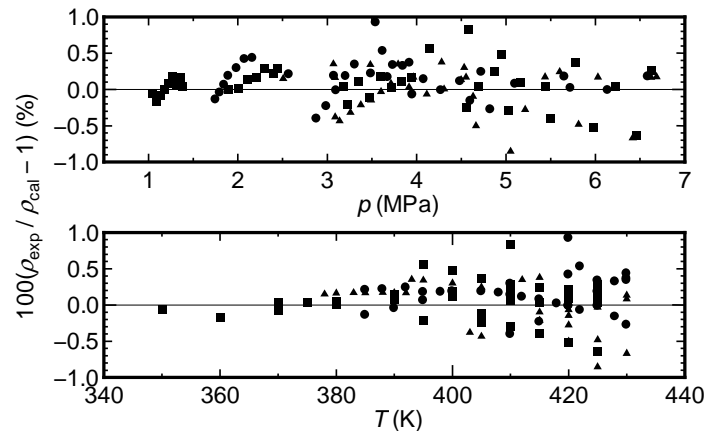


Figure 3: Deviations in the experimental densities in the single phase from the KW1 model: (●) R-134a/245fa = 10/90 mass%, (▲) 30/70 mass%, (■) 50/50 mass%.

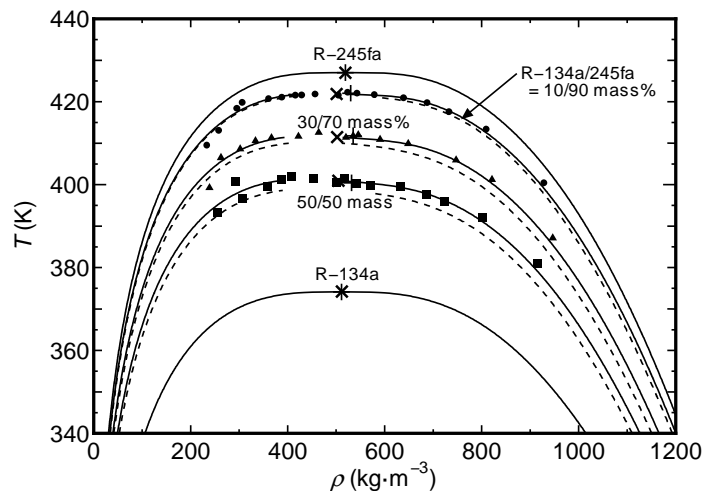


Figure 4: Phase boundaries on the  $T$ - $\rho$  diagram: (● ▲ ■) Saturated densities (this work), (---) REFPROP 9.1 (Lemmon et al., 2013), (—) KW1 model (this work), (+) Critical point (experimental), (x) Critical point (calculated).

## 5. CONCLUSIONS

Applying the multi-fluid approximation, this work successfully modeled the thermodynamic properties of the R-134a/245fa mixtures. Comparisons to experimental data including the VLE, the saturated liquid and vapor densities, the  $p$  $v$  $T$  $x$  properties, and the critical parameters shows reasonable accuracies of this property model; therefore, the model allows reliable analysis of refrigeration systems or heat pumps using the mixtures.

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